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FUNDAMENTALS OF NITRIC OXIDE FORMATION IN FOSSIL FUEL COMBUSTION

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ABSTRACT

A study of the reactions which may lead to NO formation from fuel nitrogen was continued. The volatile products formed from the pyrolysis of pyridine in an inert atmosphere were found to be HCN, vinyl cyanide, benzene, acetylene, ethylene (very small amounts) and possibly diacetylene. Significantly, no evidence of acetonitrile was found. Mass spectrometric analysis of the non-volatile tar which forms at the reactor exit, using a solid probe, indicated the presence of condensed-ring, heterocyclic aromatic and bipyridinyl groups. In addition, elemental analysis of the solid indicated that the relative nitrogen content decreased as the temperature of pyrolysis increased.

Concurrently a study of the rate of oxidation of cyanogen was started using reaction times of 0.25 to 3.00 sec. and temperatures of 950 to 1000°C. The data is still preliminary so that no conclusions have been formed as yet.

OBJECTIVE AND SCOPE

One of the major scientific problems confronting society today is the reduction and control of air pollution. The emission of NO and other oxides of nitrogen from various combustion devices is a serious contributor to that pollution. The source of NO during the combustion process may be atmospheric nitrogen or nitrogen-containing compounds in the fuel. In order to predict NO emission for the formulation of suitable analytical models, it is necessary to have accurate kinetic data and a reasonable reaction mechanism for the formation of NO.

The objective of this research program is to obtain kinetic and product distribution data from which a mechanism may be proposed for the formation of NO from fuel nitrogen. Specifically, the kinetics of the pyrolysis and oxidative pyrolysis of pyridine (since it is representative of the nitrogen-containing components of fossil fuels) will be studied. In addition, similar oxidative studies will be made on representative, condensed-ring heterocycles, e.g. quinoline, carbazole, etc. to determine the extrapolatability of the results obtained with pyridine to more coal like structures. The oxidation of volatile, nitrogen-containing pyridine pyrolysis products, e.g. cyanogen, HCN, vinylcyanide, etc., will also be carried out to help elucidate the mechanism of NO formation.

The experimental approach will involve the use of a stirred-flow reactor to obtain differential rate data which will aid in interpretation of complex kinetic data. On stream mass spectrometric, gas chromatographic and infrared spectrophotometric monitoring of products and reactants will be carried out also.

SUMMARY OF PROGRESS

Task 1 is the construction of the flow systems for the kinetic studies described in the objectives. All the components for the Quadrupole Mass Spectrometer have been received and construction has been started. The rest of the flow systems are operational.

Task 2, which consists of experiments to determine the rate and mechanism of pyrolysis of pyridine in an inert atmosphere, has been about 90% completed. This quarter's work has concentrated on the identification of volatile products obtained during the pyrolysis at 950°C and above. Four of the five product peaks obtained in the chromatograms of the samples from the reactor's exit have been identified by MS and GC. These are, in order of increasing retention time: 1. a mixture of acetylene, methane and probably a little ethylene; 2. HCN; 3. possibly diacetylene (not identified as yet); 4. vinyl cyanide; and 5. benzene. No mass spectral evidence of acetonitrile has been found although peak 3 has the same retention time as acetonitrile. In addition to the identification of the volatile products formed a shift in amount of these products was evidenced, i.e. as the temperature increased the amounts of volatile products formed increased at the same extents of reaction. Work is continuing on the characterization of these products.

Task 4, which is concerned with the oxidation of nitrogen-containing intermediate species, has been initiated with a study of the rate of oxidation of cyanogen. The investigation of this oxidation is only about 5% completed and results are still in the preliminary stages.

DETAILS OF TECHNICAL PROGRESS

Task 1

All the components of the Quadrupole Mass Spectrometer have been obtained and assembly is being initiated.

Task 2

Work concentrated on the identification of the products from the pyrolysis of pyridine, the results from which are divided into volatile and solid product analyses. The results of the pyrolysis kinetics were reported in the previous quarterly progress reports (1).

Volatile Products. The relative amounts of volatile products were very low at low operating temperatures and increased as the temperature increased. At 925°C the highest extent of reaction was 28.4% at 1 sec contact time and 2 mole % pyridine; no volatile product was detected at this condition or at lower temperatures. At 950°C and extents of reaction higher than 11% two product peaks were obtained; at 975 and 1000°C in all experiments, three additional peaks showed up.

The gas chromatographic column attached to the flow stream was normally run at 70°C. This shortened the retention time of pyridine (140 sec) and permitted faster analysis or pyridine consumption. However, at this temperature resolution between some of the volatile products was not obtained. To get a better separation, the column temperature was set at 34°C. The retention times of all the exit gases along with the compounds to which they are believed to correspond are shown in Table 1.

A sample of the volatile reaction products formed at 975°C and 65% extent of reaction, which had been trapped by liquid nitrogen, gave six

peaks when passed through the chromatograph of the mass spectrometer (LKB GC-MS instrument used through the courtesy of the Upjohn Company). The first three peaks were very close in retention time using the column in the MS, thus a mass spectrum was obtained for the composite. Mass spectra were then obtained for the last three peaks separately. The mass spectra indicated the probable constituents of the peaks in Table 1. Samples of those constituents were then passed through the column on the flow system to give the "known" data in Table 1. Work is continuing on a more complete identification.

Table 1

Gas Chromatographic Data
(34°C Column Temp.)

No.	Retention Time, (sec.) Products	Knowns	Compound
1	18	16	Acetylene and/or methane or ethylene
2	49	-	HCN[a]
3	106	-	Diacetylene[b]
4	132	130	Vinyl cyanide
5	232	230	Benzene
6	760	760	Pyridine

a) Identified by odor initially, and later mass spectrometrically.

b) Suggested by mass spectrometer data, a known was not available to check its retention time.

To more quantitatively illustrate the shift to larger amounts of volatile products at higher temperatures, it was found that at 950°C and 24% reaction, the ratio of HCN peak height to that of 1% pyridine was .05 (HCN peak height

was 5% of the peak height of 1% pyridine in the gas stream). At 1000°C and 22% reaction, the HCN peak height was 14.3% of a 1% pyridine peak height; at the same conditions the amounts of benzene and vinyl cyanide were about equal and they had peak heights of about 15% of the HCN peak.

It should be noted that acetonitrile reported as a product in earlier investigations (2), had a retention time of 109 sec and this matched with the product peak at 106 sec. However, none of the mass spectra gave a significant signal at an m/e of 41, including the mass spectra of the total gas sample. Thus it is concluded that acetonitrile is not a significant product.

Further analysis of the condensed product using a high resolution mass spectrometer (Atlas instrument, Upjohn Co.) revealed a small peak with an exact mass of 28.0314, indicating the presence of a small amount of ethylene.

Solid product. A brown, non-volatile, tar-like material formed by the reaction coated the walls of the reactor outlet; it was because of this residue that a complete mass balance was not possible. The residue was soluble in acetone and dimethylsulfoxide. According to quantitative elemental analysis, the solid product formed at 950°C, 1.00 sec residence time and 1.00% initial pyridine concentration (36% reaction) had the composition 78.6% C, 4.3% H and 16.2% N (pyridine is 75.92% C, 17.71% N and 6.37% H). At 1000°C, 1.00 sec contact time and 1.00% initial pyridine concentration (77% reaction) 85.0% C, 3.8% H and 10.4 % N were found. As the composition of the residue depends on the amount of non N containing volatile products, no conclusion could be reached as to what the theoretical N content in the residue should be. The decrease in the nitrogen content of the residue at the higher experimental temperature was consistent with the results from the previous workers (2) as most of the nitrogen was in the residue at low temperature, while essentially all of it was converted into the volatile

products, specifically HCN, as the temperature increased to 1100°C. It was also found that once the residue was formed, further heating did not produce HCN. This shows that the HCN formed in the high-temperature pyrolysis experiment forms directly in the initial pyrolysis reaction.

The infrared spectrum of the residue showed major absorptions at 2200 cm^{-1} and 1625 cm^{-1} which corresponded to C≡N and C=C stretches respectively. The NMR spectrum showed signals in the range δ = 7.6 - 8.8. This pattern is characteristic of complex aromatic compounds. The mass spectrum using the solids probe of a Dupont Model 21-490B instrument had grouped signals. Taking the most intense mass number from each group, the order in terms of decreasing relative abundance was (including the molecular structures which may have given rise to these groups of ions): 154 (biphenyl, bipyridine), 128 (napthalene, quinolines), 179 (acridine, benzoquinoline), 104 (styrene), 117 (indole), 203 (pyrene with one nitrogen in a ring), and 167 (carbazole). The following groups of ions (again only the most intense from each group is listed) also were observed and could have come from several of the above structures 51, 79, and 101. This is not intended to be a comprehensive listing of all species, but represents groups which are probably present in the solid. A full characterization of the solid would be a complete research project in itself and of questionable value for the overall objectives of this project in view of the observed trend toward a higher fraction of products as volatiles as the temperature increases.

Task 4

Task 4 consists of the oxidation of key intermediate products formed during the pyrolysis of pyridine. The flow system is essentially the same as that used for the pyridine pyrolysis except that it has two separate gas lines for oxidizer and fuel and the reactor is KCl coated, which reduced the rate of oxidation.

Cyanogen was chosen as the fuel since HCN appears to be the volatile product produced in the largest amount from the pyrolysis and it was assumed that the oxidation of the CN group would be similar for both compounds.

The fraction of cyanogen reacted was measured by recording the change in the size of the m/e = 52 peak with an MS-10 (Picker-Nuclear) as the stream passed through the reactor. From the known initial concentrations and the fraction reacted the rate of disappearance of cyanogen and apparent first-order rate constant (rate/cyanogen concentration) were calculated.

The data and results at five sets of initial concentrations and three temperatures are summarized in Table 2. It should be noted that there was no cyanogen consumption in the absence of oxygen at these conditions. If the data at 0.25/2.0 initial mole % ratio are not considered because they appear inconsistent with the other four sets of data it would be concluded that the reaction is first-order in cyanogen and zero-order in oxygen. This is only preliminary and additional data will be obtained over a larger range of concentrations.

Tasks 3, 5 and 6

These tasks will be undertaken at a later date.

Table 2

Oxidation of Cyanogen - Rate Data*

950°C

$t_c \backslash c_o$	0.5/2.0			0.25/2.0		
	%	r x 1000	r/c	%	r x 1000	r/c
0.25	2.5	4.92	.104	7.3	7.08	.315
0.5	5.4	5.20	.113	7.3	3.52	.157
1.0	8.5	4.10	.093	14.3	3.46	.167
2.0	15.7	3.82	.093	22.7	2.74	.146
3.0	23.2	3.74	.101	34.8	2.80	.178

$t_c \backslash c_o$	1.0/1.0			0.5/1.0			0.25/1.0		
	%	r x 1000	r/c	%	r x 1000	r/c	%	r x 1000	r/c
0.25	2.6	10.12	.107	2.5	4.74	.100	1.0	1.00	.041
0.5	4.3	8.36	.090	5.5	5.28	.115	9.2	4.44	.202
1.0	8.8	8.48	.096	10.6	5.16	.119	11.5	2.78	.129
2.0	14.7	7.12	.086	16.7	4.04	.100	18.2	2.22	.112
3.0	20.5	6.62	.086	24.1	3.92	.106	23.1	1.86	.100

975°C

$t_c \backslash c_o$	0.5/2.0			0.25/2.0		
	%	r x 1000	r/c	%	r x 1000	r/c
0.25	2.6	5.04	.108	5.9	5.60	.250
0.5	7.7	7.28	.166	10.6	5.06	.238
1.0	15.6	7.42	.184	18.5	4.40	.226
2.0	24.4	5.82	.164	35.5	4.22	.274
3.0	34.6	5.48	.176	48.5	3.84	.314

$t_c \backslash c_o$	1.0/1.0			0.5/1.0			0.25/1.0		
	%	r x 1000	r/c	%	r x 1000	r/c	%	r x 1000	r/c
0.25	3.5	13.22	.144	5.0	9.52	.210	2.6	2.44	.106
0.5	6.6	12.56	.142	7.8	7.42	.170	4.5	2.16	.094
1.0	14.2	13.46	.164	15.4	7.32	.182	12.0	2.86	.136
2.0	22.9	10.88	.148	27.1	6.46	.186	20.5	2.44	.128
3.0	27.6	8.76	.126	33.9	5.38	.172	28.5	2.26	.134

Oxidation of Cyanogen - Rate Data[A] (continued)

1000°C

$t_c \backslash c_o$	0.5/2.0			0.25/2.0		
	%	r x 1000	r/c	%	r x 1000	r/c
0.25	4.9	9.22	.208	15.5	14.44	.732
0.5	11.3	10.52	.254	16.8	7.82	.402
1.0	20.3	9.48	.256	29.1	6.78	.412
2.0	35.0	8.16	.268	44.1	5.16	.394
3.0	50.2	7.80	.336	58.6	4.56	.472

$t_c \backslash c_o$	1.0/1.0			0.5/1.0			0.25/1.0		
	%	r x 1000	r/c	%	r x 1000	r/c	%	r x 1000	r/c
0.25	5.5	20.46	.232	6.5	12.08	.278	4.4	4.06	.182
0.5	12.6	23.44	.288	11.6	10.82	.262	9.1	4.22	.200
1.0	19.2	17.94	.238	21.3	9.92	.270	17.8	4.14	.216
2.0	29.7	13.88	.212	33.2	7.74	.248	31.0	3.62	.224
3.0	33.9	10.56	.172	43.4	6.76	.256	48.9	3.80	.318

[A]The symbols have the following significance:

t_c = contact time (sec).

c_o = reactor entrance concentrations (mole % in helium, $(CN)_2/O_2$).

% = percent cyanogen reacted.

r = rate of cyanogen consumption (mmoles/l·sec).

r/c = apparent first-order constant for cyanogen consumption (sec^{-1}).

REFERENCES

(1) (a) T. Houser, " Fundamentals of Nitric Oxide Formation in Fossil Fuel Combustion" , ERDA, FE-2018-1, QPR Period June-September 1975.

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(b) C.D. Hurd and J.I. Simon, J. Am. Chem. Soc., 84, 4519 (1962).